

STUDIES OF THE ELECTRONIC PROPERTIES OF POINT DEFECTS IN SEMICONDUCTORS

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This thesis is based on the following papers:

- A. S.T.Pantelides and J.Bernholc: "Theory of Photoionization Cross Sections of Impurities in Semiconductors" in "Radiation Effects in Semiconductors 1976" ed. by N.B.Urli and J.W. Corbett (Institute of Physics, London), p 465.
- B. J.Bernholc and S.T.Pantelides: "Theory of Binding Energies of Acceptors in Semiconductors"
Phys.Rev. B 15, 4935 (1977)
- C. J.Bernholc and S.T.Pantelides: "Scattering - Theoretic Techniques for Defects in Semiconductors - Ideal Vacancies in Si, Ge and GaAs" to be published.

INTRODUCTION

Matter can appear in three basic states: gaseous, liquid and solid (a fourth state the so-called plasma state is sometimes introduced nowadays).

In a gas atoms move freely and independently of each other. If the temperature is lowered and/or the pressure increased, the gas will condense to a liquid and finally at still lower temperature and/or higher pressure the positions of the atoms become frozen, a solid is formed.

The formation of a solid may be microscopically understood in the following way. Imagine an assembly of atoms far apart from each other. Every atom consists of a nucleus surrounded by a cloud of electrons moving around the nucleus in elliptical orbits. The energy spectrum of an atom is discrete, and the most tightly bound electrons have lowest energy. They are called core-electrons. The outer electrons, capable of forming chemical bonds, are called valence electrons.

When the atoms approach each other, electrons belonging to different atoms will start to interact, and the discrete atomic energy levels will be broadened into bands, separated by energy gaps. The valence electrons will form bonds between the atoms, whereby the total energy of the system is lowered. At short interatomic distances, however, core electrons also interact with each other, which, since all core levels are filled, results in a repulsion. An equilibrium state is then formed with atoms at fixed positions, with the atoms only angstroms apart. The gain in total energy is of the order of a few electronvolts per atom, which explains, why solids can be formed only when the temperature is low enough.

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The research conducted in this thesis is concerned with solids and belongs to a vast branch of physics called solid state physics. One important aim of solid state physics is the understanding of macroscopic properties of solids in terms of its microscopic constituents, i.e. electrons, protons and neutrons.

Solids can be classified in various ways. A very common classification is based on their ability to conduct electricity. The simple model described above is also capable of explaining the great difference between the electrical properties of metals, semiconductors and insulators.

Metals are formed when the highest occupied level of the corresponding atom is only partially filled, or when an unoccupied and an occupied level cross upon broadening. In both cases the highest occupied band is only partially filled, whereby the electrons belonging to this band can be easily driven by the electric field and conduct electricity. In semiconductors and insulators at zero temperature, on the other hand, the highest occupied band, the valence band, is completely filled, and is separated from the nearest empty band, the conduction band by a band gap E_g . When a band is completely filled, the electrons cannot move and the conductivity is then zero.

At room temperature, however, some electrons can be thermally excited from the valence band to the conduction band, leaving behind holes in the valence band, which behave as positively charged particles. The electrons in the conduction band and the holes in the valence band are free and can conduct electricity.

The number of electrons in the conduction band and the number of holes in the valence band follows Boltzmann statistics and is proportional to $\exp(-E_g/2kT)$.

In insulators, the band gap E_g is large and thus the number of conduction electrons is small. The conductivity is still almost zero at room temperature.

Semiconductors, on the other hand, have much smaller band gaps, and the number of conduction electrons at room temperature is substantially larger. Since the conductivity is proportional to the number of carriers, it should increase with temperature as $\exp(-E_g/2kT)$ in a semiconductor. This is easily observed experimentally.

The conductivity of a semiconductor can be substantially altered by the presence of a small amount of foreign atoms, so-called impurities. In fact, impurities in concentrations less than one per million can change the conductivity of silicon by several orders of magnitude. Furthermore, depending on the type of the impurity, the carriers will predominantly be electrons (n-type material) or holes (p-type material). This phenomenon can be microscopically understood as follows.

Consider an atom belonging to the fifth column of the periodic table of elements. Such an atom has five valence electrons, and, when substituted in place of a fourvalent silicon atom, there is one electron left over. This electron will then be bound by a potential $V(r) = -e^2/\epsilon r$ where ϵ is the dielectric constant of silicon. The effect of the surrounding silicon atoms on the motion of this electron can be simulated by replacing its real mass by the so-called effective mass m^* in the equation of motion. With this assumption the problem is isomorphic to that of the hydrogen atom. The electron in its ground state will move around the impurity in an extended hydrogenic orbit with an effective Bohr radius of ϵ/m^* atomic units, which in silicon is of the order of $15\text{\AA}$. Energetically, this state will be situated $m^*/\epsilon \times 13.6$ eV below the conduction band edge. This energy is typically 10-100 meV, therefore, at room temperature, a substantial fraction of all the extra

electrons will be excited into the conduction band, where they are free to conduct electricity.

In this way, the number of electrons in the conduction band at room temperature can easily be controlled by doping with group V impurities.

Let us now consider a group III impurity. It has only three valence electrons, therefore, when placed on a silicon position, it can only contribute to three of the four bonds. The missing electron is taken from the valence band, leaving a hole of charge $+e$. This hole is bound by the potential of the form $V(r) = -e^2/\epsilon r$. Defining the effective mass for holes in an analogous way, one obtains, that the ground state of the hole lies above the valence band edge, the distance being of the order of 10-100 meV.

At room temperature, the bound hole states will be ionized into the valence bands. The hole conductivity can therefore be controlled by doping with group III impurities.

Impurities which donate electrons to the conduction band, are called donors, while those which accept electrons from the valence band are called acceptors. A donor with ground state energy close to the conduction band edge, or an acceptor with ground state energy close to the top of the valence band, are called shallow. Impurities which have energy levels in the middle of the gap are called deep. Such impurities have often both acceptor states and donor states.

Group V impurities are always shallow donors in silicon, group III impurities are always shallow acceptors. They both replace a silicon atom on its lattice position, therefore they are called substitutional. Shallow donors and acceptors are reasonably well described by the Effective-Mass Theory (EMT), which in its simplest version was described above.

Substitutional group VI and II impurities are double donors and double acceptors, respectively. One would expect the effective mass theory to be valid even in this case. The EMT however, predicts the binding energy of the second electron be the four times larger, while the experimentally measured ionisation energies are much greater.

Recently, Pantelides and Sah have generalized the effective-mass theory. By using atomic pseudopotentials and by including the proper dielectric screening they have been able to obtain binding energies of single and double donors in silicon in good agreement with experimental observations. The chemical shifts, i.e. the differences between binding energies of various single and double donors have also been correctly reproduced.

In paper B this theory is applied to acceptors in silicon, germanium and a number of compound semiconductors. It is concluded, that the effective-mass theory is applicable to single and double acceptors in silicon, as well as to single, double and triple acceptors in germanium. In compounds, however, effective-mass theory can only be applied to very shallow levels. For deeper levels, effects due to differences in the anion and cation sites are dominant. These effects cannot be included in the effective-mass theory.

Generally, defect states where most of the binding energy arises from a short-range potential cannot be treated by the effective-mass theory. Such defects include transition metal impurities, vacancies, isovalent impurities i.e. impurities with the same number of valence electrons as the host atoms they replace, and some other defects. Also defects accompanied by lattice distortions, for instance those caused by an exceptionally large or small size of the impurity atom, e.g. gold in silicon or oxygen in gallium phosphide, are outside the realm of the EMT.

The non-EMT-like defects are usually quite deep. The solubility of those defects is low, and they have no substantial effect on the number

of free carriers. However, they often act as very efficient recombination centers, therefore they determine the lifetime of the carriers. In this way the non-equilibrium or transient conductivity is controlled by the number and kind of deep defects present in the sample.

In contrast to shallow and those intermediately deep defects which can be described by the effective-mass theory, the electronic structure of deep non-EMT-like defects is rather poorly understood at present.

A number of models for calculation of electronic properties of deep defects has been proposed in the literature. Perhaps the most widely used model is the molecular cluster model, in which the crystalline environment of a defect is represented by a number of host atoms surrounding the defect. A wealth of information has been obtained from this model. In particular one learned that the wavefunction of a deep defect is quite extended in space, even if the defect potential is very localized. The defect wavefunction will therefore interact with surface states, unless the cluster is large enough to fully separate the defect from the surface. In practice, very large clusters are needed in order to satisfy the last condition.

One can avoid surface problems by applying periodic boundary conditions to the cluster. The defect is then repeated in space and an array of defects is formed. The defects will then interact with each other, which manifests itself in a broadening of the impurity level. An impurity band is formed. Again very large clusters are needed in order to make the defects not to interact.

A method completely different in spirit was proposed by Koster and Slater. They assume that the perfect crystal solutions are known and use the properties of those solutions to solve the problem of one isolated defect in an infinite solid. The Koster-Slater approach has several

advantages over the other two methods for calculations of electronic properties of deep levels. In contrast to the cluster method, the size of the problem in the Koster-Slater method is given by the range of the potential of the defect which is often substantially smaller than the extension of the impurity wavefunction. Also, the Koster-Slater method yields wavefunctions which automatically satisfy the correct boundary conditions, and energy levels that easily can be allocated with respect to the perfect crystal band edges.

The Koster-Slater method was generalized in the framework of formal scattering theory by Callaway, and the first realistic applications were made by Callaway and Huges. Most of the theoretical development as well as the calculations were carried out in the basis of Wannier functions. The Wannier functions, however, which are very useful for formal arguments, turned out to be very difficult to construct numerically. This resulted in a rather heavy computational scheme. For that reason only few applications have been made.

In paper C a method based on the Koster-Slater approach is presented and applied to ideal (i.e. unreconstructed) vacancies in Si, Ge and GaAs. The use of Wannier functions, however, is avoided. The method is reformulated in terms of any complete set of basis functions, which may be chosen in a way facilitating the computation of both the Green function and the potential matrix elements. The Green function matrix elements are then calculated by standard k-space integration techniques. A very efficient computational scheme is developed, which utilizes both the short-range nature of the deep-defect potential and the periodicity of the perfect crystal. We think our method is the most efficient one available at present for studying deep defects.

Experimental information on defect states is obtained from electrical, thermal and optical measurements or combinations of these methods.

A very useful experiment is to shine light of a well controlled frequency on the sample, and measure photoabsorption or photocurrent. For shallow impurities, one observes sharp transitions between the ground state and excited states as well as ground-state to band-continuum excitations which give rise to a continuous absorption curve proportional to the photoionization cross section of the impurity. Energies of the excited states can be accurately obtained from effective-mass theory, therefore very accurate binding energies of shallow impurities can be extracted from photoabsorption measurements.

The photoionization cross section provides information on the ground state wavefunction and serves as a test for various theoretical models for the impurity wavefunction. For deep defects, the transitions to the excited states are seldom resolved, and the binding energy of the deep state has to be extracted from the photoionization cross section.

In the theoretical analysis of the photoionization cross section, it is assumed that the density of states (DOS) in the continuum can be obtained from assuming a parabolic and isotropic band.

In paper A this assumption is analyzed for acceptors and found to be inadequate. New calculations are presented which for the first time take into account the details of the valence bands and make use of the Bloch functions for band states.

Finally, one should stress that our interest in the fundamental properties of semiconductors is not purely academic. Semiconductor technology, which has so profound an impact on our life, has its roots in the very basic properties of semiconductors. The action of solid state rectifiers, transistors, light emitting diodes, integrated circuits, solar cells, solid state lasers, or the final products like radios, computers, tv-sets, electronic calculators and watches depends on the kind, number and spatial distribution of various shallow and deep impurities. For that reason, the

fundamental research in semiconductors is carried out not only at universities and research institutes, but also at many large industrial laboratories like AEG, Bell, IBM, Phillips and RCA.

Such investigations result in a deeper understanding of the fundamental processes in semiconductors, and thus are also of great importance for the practical development of new and more efficient devices.

SUMMARY OF THE PAPERS

A. Previous approaches to the calculation of photoionization cross sections are reviewed and found to be inadequate. New calculations are presented which, for the first time, take into account the details of the valence bands and make use of Bloch functions for band states. The localized wavefunctions are chosen to satisfy symmetry requirements, and are then determined by reproducing experimental data. The method proves successful for a variety of shallow and deep impurities.

B. Acceptor binding energies are calculated using the full 6×6 effective mass acceptor Hamiltonian for both shallow and deep levels. It is found that for homopolar semiconductors (Si and Ge) the method is valid for both shallow and deep acceptors, in agreement with a similar result obtained previously by Pantelides and Sah for donors in Si. Screening the impurity potential by the dielectric function $\epsilon(q)$ is again found to be very important. The point-charge model is found to be adequate for shallow single acceptors and the relatively shallow double acceptors in Ge, but completely inadequate for the deep double acceptors in Si and triple acceptors in Ge. Use of model potentials, however, which reflect the chemical nature of individual impurities, is shown to be capable of reproducing the observed values. When model potentials from the literature are used, agreement with experiment is only modest, due to a sensitivity of the calculation on the core part of the impurity potential. Similar calculations in heteropolar semiconductors (GaP, GaAs, etc) show that good agreement is obtained only for very shallow levels. For deeper

levels, effects due to differences in the anion and cation sites are dominant. It is argued that these effects lie outside the effective-mass theory.

C. A technique for an accurate and efficient calculation of point defect-induced changes in the electronic structure of an otherwise perfect crystal is described. It is based on the Green's-function method introduced by Koster and Slater and developed further by Callaway and coworkers and achieves its efficiency and convenience by avoiding the use of Wannier functions. The efficiency and accuracy of the method is exhibited by calculating the states of a widely studied model system, namely the ideal vacancy in covalent solids, using semiempirical, but realistic host energy-band structures. Results for the vacancy in Si, Ge and GaAs compare favorably with those obtained previously. In addition, a wealth of new information is obtained. It is argued that the present method is the most efficient technique available for the study of deep-level impurities and defects in semiconductors--the efficiency stemming from an exploitation of both the short-range nature of the defect potential and the translational symmetry of the host crystal.

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